Knight: Chapter 18

The Micro/Macro Connection

(*Thermal Interactions and Heat & Irreversible Processes and the 2nd Law of Thermodynamics*)

Last time…

- Thermal energy of a *Monatomic gas*..

$$E_{th} = \frac{3}{2}NK_BT = \frac{3}{2}nRT$$
$$C_V = \frac{3}{2}R = 12.5\ \mathrm{J/mol\ K}$$

- Thermal energy of a *Solid*..

$$E_{th} = 3Nk_BT = 3nRT$$
$$C = 3R = 24.9\ \mathrm{J/mol\ K}$$

- Thermal energy of a *Diatomic gas*..

$$E_{th} = \frac{5}{2}Nk_BT = \frac{5}{2}nRT$$
$$C_V = \frac{5}{2}R = 20.8\ \mathrm{J/mol\ K}$$

TABLE 17.4 Molar specific heats of gases (J/mol K)

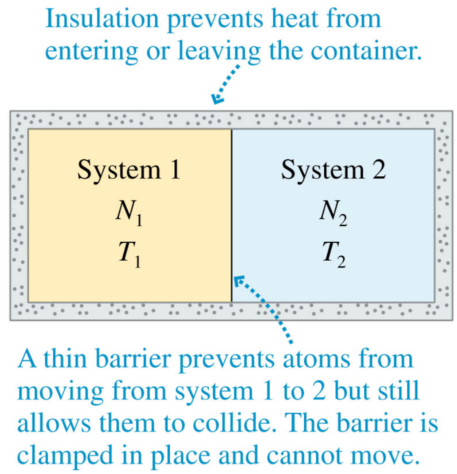
Gas	C_P	C_V	$C_P - C_V$
Monatomic Gases			
He	20.8	12.5	8.3
Ne	20.8	12.5	8.3
Ar	20.8	12.5	8.3
Diatomic Gases			
H_2	28.7	20.4	8.3
N_2	29.1	20.8	8.3
O_2	29.2	20.9	8.3

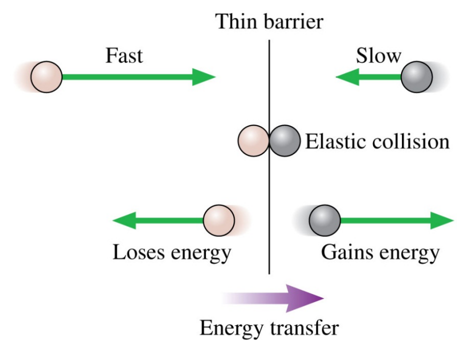
TABLE 17.2 Specific heats and molar specific heats of solids and liquids

Substance	*c* (J/kg K)	*C* (J/mol K)
Solids		
Aluminum	900	24.3
Copper	385	24.4
Iron	449	25.1
Gold	129	25.4
Lead	128	26.5
Ice	2090	37.6
Liquids		
Ethyl alcohol	2400	110.4
Mercury	140	28.1
Water	4190	75.4

Thermal interactions & heat

- Consider two gases, initially at different temps $T_{1i} > T_{2i}$.
- They can interact *thermally* through a very thin barrier.
  - Atoms collide at the boundary as if the membrane were not there, yet atoms cannot move from one side to the other.
- During the collision, there is an *energy transfer* from the faster atom's side to the slower atom's side.
- *Heat* is the energy transferred via collisions between the *more-energetic atoms* on one side and the *less-energetic atoms* on the other.





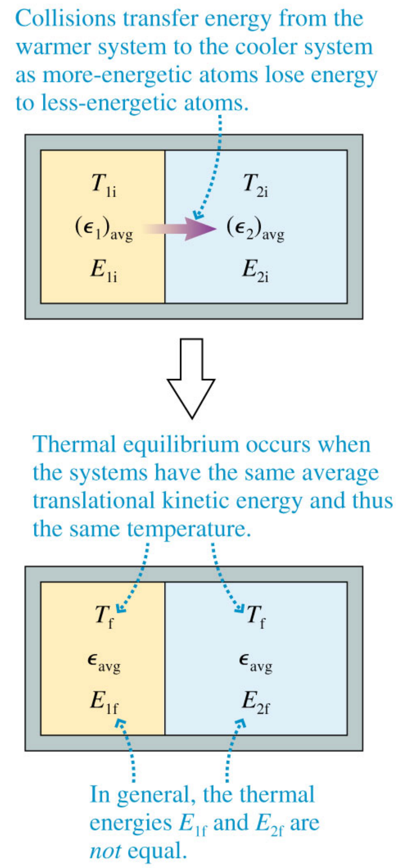
Thermal interactions & heat

- *Thermal equilibrium* is reached when the atoms on each side have, *on average*, equal energies…

$$\boxed{(\epsilon_1)_{avg} = (\epsilon_2)_{avg}}$$

- Because the average energies are directly proportional to the final temperatures…

$$\boxed{T_{1f} = T_{2f} \equiv T_f}$$



Thermal interactions & heat

The final thermal energies of the two systems are…

$(\varepsilon_1)_{Avg} = (\varepsilon_2)_{Avg}$

using the fact that

$E = N\varepsilon$

$$\frac{E_{1f}}{N_1} = \frac{E_{2f}}{N_2} = \frac{E_{TOT}}{N_1 + N_2}$$

$n = N/N_A$

$$\therefore \; E_{1f} = \frac{N_1}{N_1+N_2} E_{TOT} = \frac{n_1}{n_1+n_2} E_{Tot}$$

$$E_{2f} = \frac{N_2}{N_1+N_2} E_{TOT} = \frac{n_2}{n_1+n_2} E_{Tot}$$

NO work is done on either system, so the *1st law of thermo* is…

$\Delta E_{th} = W + Q \qquad W = 0$

$$\therefore \; \Delta E_{TH_1} = Q_1 = E_{1f} - E_{1i}$$

$$\Delta E_{TH_2} = Q_2 = E_{2f} - E_{2i}$$

Conservation of energy requires that…

$$Q_1 + Q_2 = 0$$

$$E_{1f} - E_{1i} + E_{2f} - E_{2i} = 0$$

$$\frac{N_1}{N_1+N_2} E_{TOT} + \frac{N_2}{N_1+N_2} E_{TOT} - (E_{1i} + E_{2i}) =$$

$$E_{TOT} - (E_{1i} + E_{2i}) = 0$$

Thermal interactions & heat

The final thermal energies of the two systems are…

$$E_{1f} = \frac{N_1}{N_1 + N_2} E_{tot} = \frac{n_1}{n_1 + n_2} E_{tot}$$

$$E_{2f} = \frac{N_2}{N_1 + N_2} E_{tot} = \frac{n_2}{n_1 + n_2} E_{tot}$$

NO work is done on either system, so the *1st law of thermo* is…

$$Q_1 = \Delta E_1 = E_{1f} - E_{1i}$$

$$Q_2 = \Delta E_2 = E_{2f} - E_{2i}$$

Conservation of energy requires that…

$$\boxed{Q_1 = -Q_2}$$

i.e. 18.8:
A thermal interaction

A sealed, insulated container has 2.0 g of helium at an initial temperature of 300 K on one side of a barrier and 10.0 g of argon at an initial temperature of 600 K on the other side.

a. How much heat energy is transferred, and in which direction?
b. What is the final temperature?

He = 1 Ar = 2

$m_1 = 2.0 \times 10^{-3}$ kg $t_{1_i} = 300$ K $E = \frac{3}{2} nRT$

$m_2 = 10.0 \times 10^{-3}$ kg $t_{2_i} = 600$ K

$E_{1i} = \frac{3}{2} n_1 R T_{1i} = \frac{3}{2}(\frac{1}{2} \text{mol})(8.31 \text{J/molK})(300\text{K}) = 1{,}870$ J

$n_1 = \frac{M}{m} = \frac{2.0 \times 10^{-3} \text{kg}}{4.0 \times 10^{-3} \text{kg/mol}} = \frac{1}{2}$ mol

$E_{2i} = \frac{3}{2} n_2 R T_{2i} = 1{,}870$ J

$n_2 = \frac{M}{m} = \frac{10.0 \times 10^{-3} \text{kg}}{40 \times 10^{-3} \text{kg/mol}} = 0.28$ mol

$E_T = E_{1i} + E_{2i}$

$E_{1f} = \frac{n_1}{n_1 + n_2} E_T = 2490$ J

$Q_1 = E_{1f} - E_{1i} = 2490\text{J} - 1870\text{J} = 620$ J

$E_{2f} = \frac{n_2}{n_1 + n_2} E_T = 1250$ J

$Q_2 = E_{2f} - E_{2i} = 1250\text{J} - 1870\text{J} = -620$ J

Argon $\xrightarrow{\text{to}}$ Helium $Q = 620$

$\Delta E_{th} = W$

$\Delta E_{th\,1} = \frac{3}{2} n_1 R \Delta T_1 = Q_1$ $\Delta T_1 = \frac{Q_1}{\frac{3}{2} n_1 R} = 400$ K

$\Delta E_{th\,2} = \frac{3}{2} n_2 R \Delta T_2 = Q_2$ $\Delta T_2 = \frac{Q_2}{\frac{3}{2} n_2 R} = 400$ K

Irreversible processes and the 2nd law of thermodynamics…

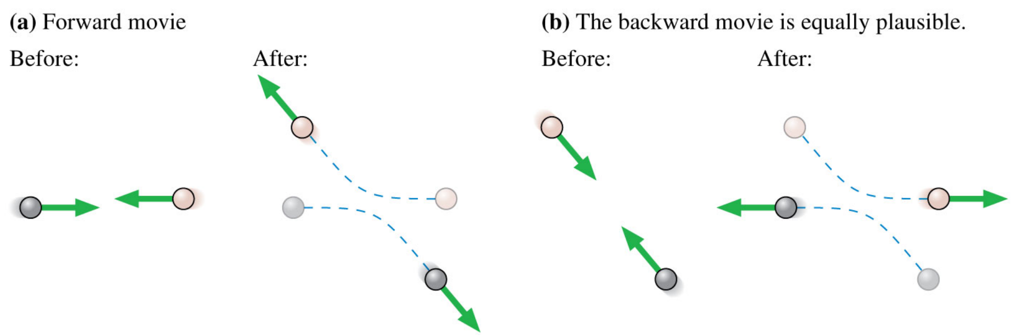
- When two gases are brought into thermal contact, heat energy is transferred *from the warm gas to the cold gas* until they reach a common final temperature.

- Energy could still be conserved if heat was transferred in the opposite direction, but this *never happens*.

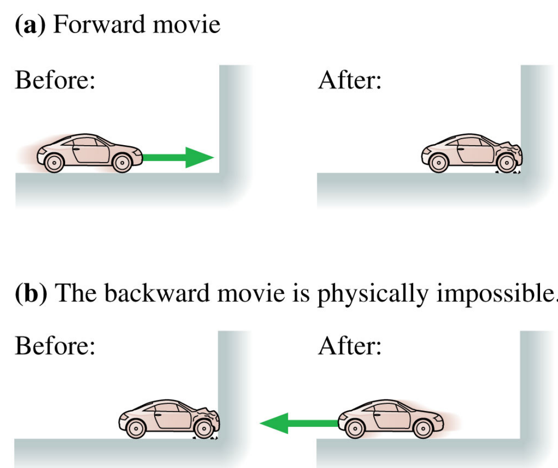
- The transfer of heat energy from hot to cold is an example of an *irreversible process*, a process that can happen *only* in one direction.

Irreversible processes and the 2nd law of thermodynamics…

Molecular collisions are *reversible*…



A car crash is *irreversible*…

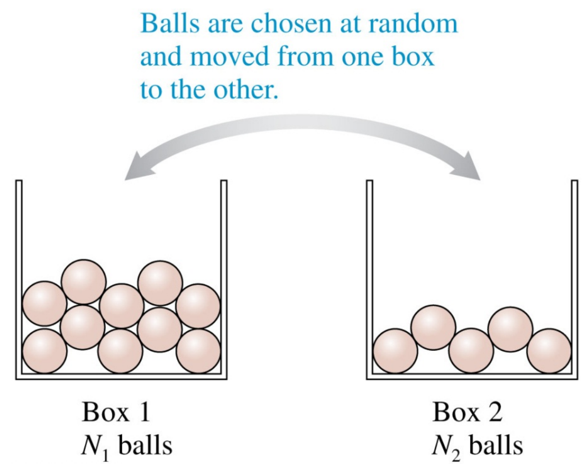


Which way to equilibrium?

- The figure shows 2 boxes containing identical balls.
- Once every second, one ball is chosen at random and moved to the other box.
- What do you expect to see if you return several hours later?

- Although each transfer is *reversible*, it is more likely that the system will evolve toward a state in which $N_1 \approx N_2$ than toward a state in which $N_1 >> N_2$.

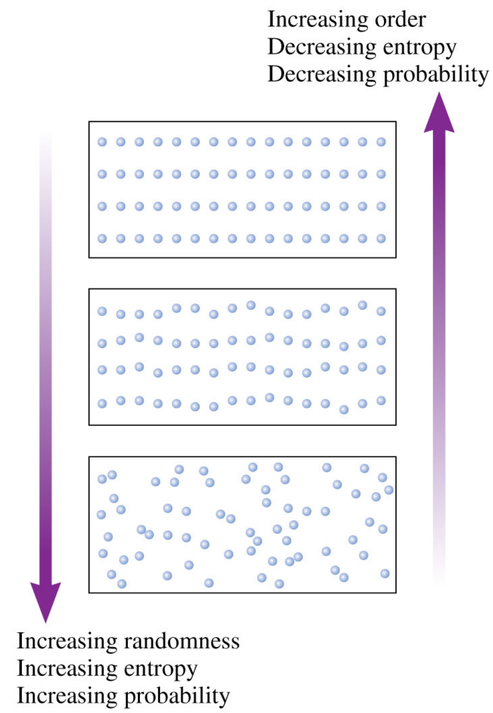
- The macroscopic drift toward equilibrium is *irreversible*.



Order, disorder, and entropy…

Entropy…

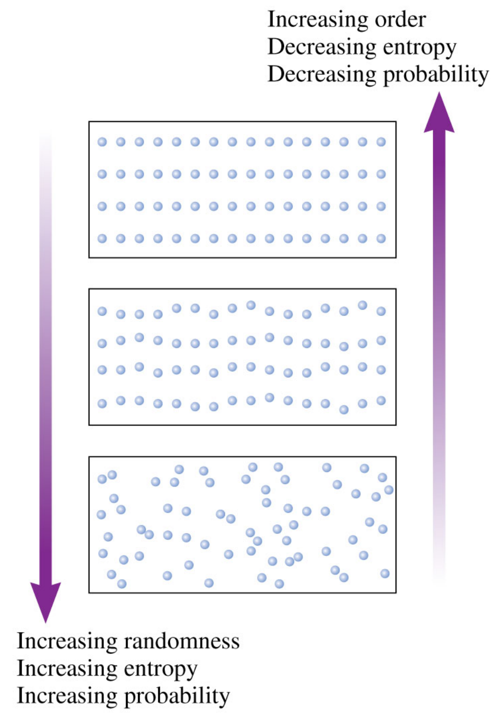
- is a *state variable* that measures the *probability that a macroscopic state will occur spontaneously*.
- measures the amount of *disorder* in a system.



Order, disorder, and entropy…

Throw N coins in the air and let them fall…

- Any # of heads are possible.
- Throw four coins…
  - Odds are 1 in 2^4, or 1 in 16 of getting four heads; this represents fairly *low entropy*.
- Throw 10 coins…
  - Odds that $N_{heads} = 10$ is $0.5^{10} \approx 1/1000$, which corresponds to *much lower entropy*.
- Throw 100 coins…
  - Odds that $N_{heads} = 100$ has dropped to 10^{-30}; it is safe to say it will never happen.



- Entropy is *highest* when $N_{heads} \approx N_{tails}$.

2^{nd} Law of Thermodynamics…

Macroscopic systems evolve *irreversibly* toward equilibrium..

The entropy of an isolated system (or group of systems) never decreases. The entropy either increases, until the system reaches equilibrium, or, if the system began in equilibrium, stays the same.

This law tells us what a system does *spontaneously* without outside intervention.

2^{nd} Law of Thermodynamics…

The 2nd law is often stated in several equivalent but more informal versions:

Informal statement #1:

When two systems at *different* temperatures interact, heat energy is transferred spontaneously *from the hotter to the colder*, never from the colder to the hotter.

Informal statement #2:

The time direction in which the entropy of an isolated macroscopic system increases is the future.

Establishing the "arrow of time" is one of the most profound implications of the 2^{nd} law of thermodynamics!